MONTE CARLO STUDY OF THE MAGNETOELASTIC PROPERTIES OF FE-NI CLUSTERS

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1 Introduction

The search for new properties of materials composed of clusters (cluster-assembled materials) or of small nanoparticles has reached a state of technological importance. Moreover the evolution of the magnetic properties from the atom to the bulk via cluster growth is itself a fascinating and challenging problem. However, in spite of considerable effort spent on the investigation of the magnetic properties of metal clusters,[1-7] a coherent understanding of this subject has not yet been established. In this paper we study a feature of particular interest namely the magnetoelastic properties of small clusters composed of iron and nickel. It is known that alloys of these elements are characterized by outstanding anomalies regarding their structural and magnetoelastic properties on the iron-rich side of the phase diagram. Especially for compositions around 35 at.% Ni experiments reveal vanishing thermal expansion around room temperature, the so-called Invar effect, which has been the subject of numerous experimental and theoretical investigations since its discovery.[8-11] At slightly lower Ni concentrations, in addition to the magnetic anomalies, structural instabilities appear since the alloy undergoes a martensitic transformation from the fcc to the bcc phase.[12,13]

An early phenomenological explanation of the Invar effect was given by Weiss[14] who proposed that in fcc iron two different electronic states could coexist: One in which the electronic orbitals are filled without obeying Hund's rule characterized by the low magnetic moment (LM) and a smaller lattice parameter and the other in which Hund's rule is obeyed with high magnetic moment (HM) and a larger lattice parameter. Considering the HM state to be the fundamental state, one can explain the anomalous thermal expansion behavior by a gradual transition from the HM state to the LM state with increasing temperature. Thus the usual thermal expansion is compensated by reducing the volume as the fraction of iron atoms in the LM state

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increases. Considerations of this kind have also been supported by band structure calculations,[15-17] which prove the existence of two minima on the binding surface corresponding to LM and HM lattice constants. Furthermore the difference in energy between these minima is found to be well in the range of thermal fluctuations.

Assuming that the HM-LM aspect is the most important feature of Invar systems like Fe-Ni, we study the magnetoelastic properties of these alloys by using an Ising-like spin model with coupled magnetic and lattice degrees of freedom. For the bulk case this model has been investigated by Gruner et al.[18,19] with a constant pressure Monte Carlo method. In this work we will use the same finite-temperature Monte Carlo method in order to study the thermodynamic and magnetoelastic properties of small clusters of iron and nickel.

2 The model

In order to assign the LM and HM state to the Fe atom, we consider a modified spin-1 Ising model with $S_i = \pm 1$ for the HM state and $S_i = 0$ for the LM state. Furthermore we allow the statistical weight of the LM state to vary, which determines the fraction of LM spins in the high temperature limit. Since pure nickel does not exhibit the above mentioned anomaly in its thermal expansion curve, we can neglect the LM state for nickel atoms and represent the spin of nickel atoms by using Ising-spins with $S_i = \pm 1$. We take into account the magnetovolume effect through spin-dependent pair potentials of Lennard Jones type. For the sake of simplicity the pair potentials are assumed to be the same for iron and nickel. The total model Hamiltonian is then

$$H = -\sum_i D_i S_i^2 - \sum_{<ik>} J_{ik} S_i S_k + \sum_{<ik>} U(r_{ik}, S_i S_k), \tag{1}$$

where D_i are crystal field constants which separate the HM and LM states energetically. $J_{ij} = J_{\mathrm{Fe-Fe}}$, $J_{\mathrm{Fe-Ni}}$ and $J_{\mathrm{Ni-Ni}}$ are the exchange constants of the interaction between Fe-Fe, Fe-Ni and Ni-Ni atoms, respectively. The summation is performed over pairs of nearest neighbors. For the pair potentials we use

$$U(r_{ik}, S_i, S_k) = \begin{cases} 4\,\epsilon_{\mathrm{L}} \left(\left(\frac{d_{\mathrm{L}}}{r_{ik}} \right)^{12} - \left(\frac{d_{\mathrm{L}}}{r_{ik}} \right)^{6} \right), & S_i S_k = 0 \\ 4\,\epsilon_{\mathrm{H}} \left(\left(\frac{d_{\mathrm{H}}}{r_{ik}} \right)^{12} - \left(\frac{d_{\mathrm{H}}}{r_{ik}} \right)^{6} \right), & S_i S_k \neq 0 \end{cases}, \tag{2}$$

where $\epsilon_{L,H}$ denotes the lattice energy at the equilibrium distances $r_{ik} = 2^{1/6} d_{L,H}$ between two nearest neighbor atoms for LM and HM potentials, respectively.

3 Simulation method

Recent experimental investigations[6] indicate that fcc-Fe nanoparticles of size less than 100 nm do not undergo a martensitic transformation when the temperature is reduced to 4.2 K. This shows that at very low temperature the fcc lattice structure is stable for the case of small Fe-clusters. Therefore, it is reasonable to assume a fcc lattice structure for our systems (which is of the size $2 \ldots 6$ nm). In this work we performed a finite-temperature Monte Carlo simulation to study the Hamiltonian (1) using open boundary conditions. Our Monte Carlo routine consists of local update steps for spin and lattice degrees of freedom, respectively. First a new spin state is chosen using the usual Metropolis algorithm in order to simulate the spin configuration. Afterwards we include the vibrational degrees of freedom by moving the lattice site to a new trial position from a cubic region around the actual position. Again this new position is accepted or rejected according to the Metropolis criterion. In order to improve the convergence, the size of the cube is determined by the condition that about half of the proposed moves is accepted. For our calculation 160 000 to 320 000 lattice sweeps are performed for each temperature starting with the final configuration of the previous temperature. The first 40 000 steps are used to allow the system to reach equilibrium. Finally for each temperature we have averaged over 4 to 15 different random distributions with a fixed composition of iron and nickel atoms. Sample configurations of particles with different sizes are shown in Fig. 1.

In order to be able to compare the results with the simulations of bulk Fe-Ni alloys we used the same set of parameters when simulating nanoparticles. The magnetic parameters have been fixed to $J_{\mathrm{Fe-Fe}} = -0.72\,\mathrm{mRy}$, $J_{\mathrm{Fe-Ni}} = 0.96\,\mathrm{mRy}$ $J_{\mathrm{Ni-Ni}} = 0.40\,\mathrm{mRy}$ and $D_{\mathrm{Fe}} = -2.20\,\mathrm{mRy}$. We choose $D_{\mathrm{Ni}} \gg k_{\mathrm{B}}T$ in order to prevent nickel spins from switching to the LM state. Please note that the Fe-Fe exchange constant favors antiferromagnetic spin order while the others prefer parallel alignment of the spins. The elastic parameters are $d_H = 2.209$ Å, $d_L = 2.165$ Å and $\epsilon_H = \epsilon_L = 25.47\,\mathrm{mRy}$. Finally we set the statistical weight of the non-magnetic state to $g = 0.5$ in order to restrict the fraction of non-magnetic iron sites at infinite temperature to 20 %. The choice of the parameters, which is based on results of band structure calculations,[17,20] has been explained in detail in Ref. 19.

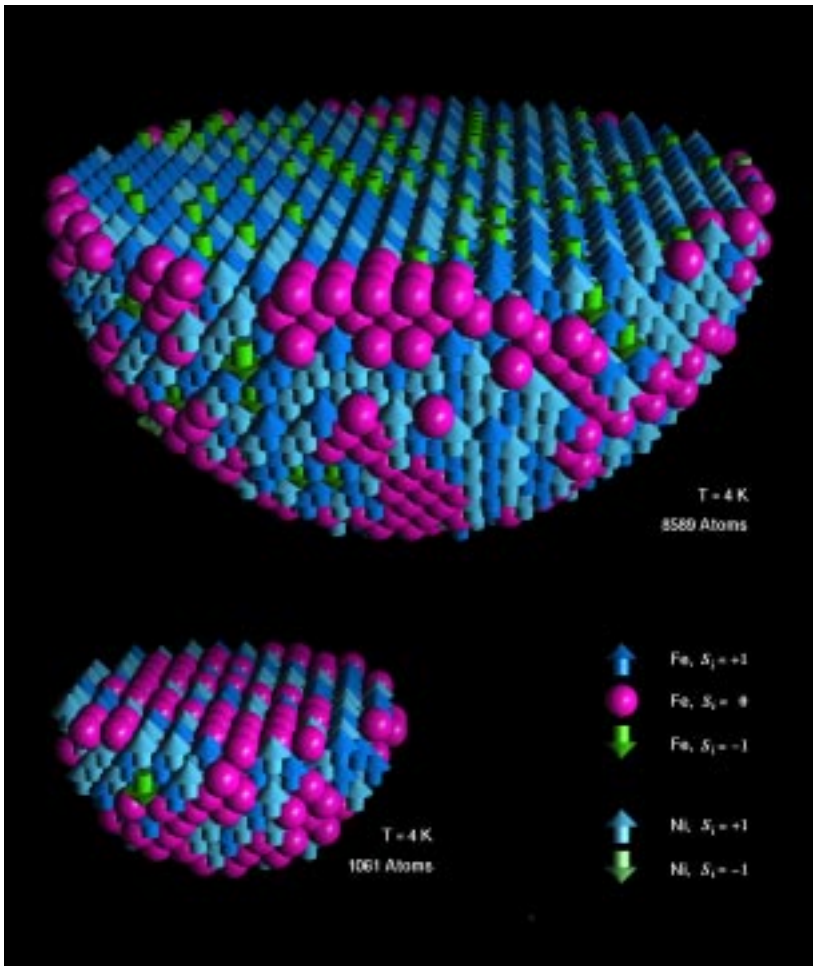

Figure 1. Sample configurations of $Fe_{65}Ni_{35}$ particles with 8589 atoms (upper panel) and 1061 atoms (lower panel) at $T = 4$ K. In order to illustrate the behavior of the inner part, the particle is cut through the center. The lighter arrows denote nickel atoms, the darker ones HM iron atoms with $S = \pm 1$. The spheres refer to LM iron.

4 Results

First we have investigated the change in the magnetoelastic behavior of particles at the classical Invar composition $Fe_{65}Ni_{35}$ when decreasing the particle

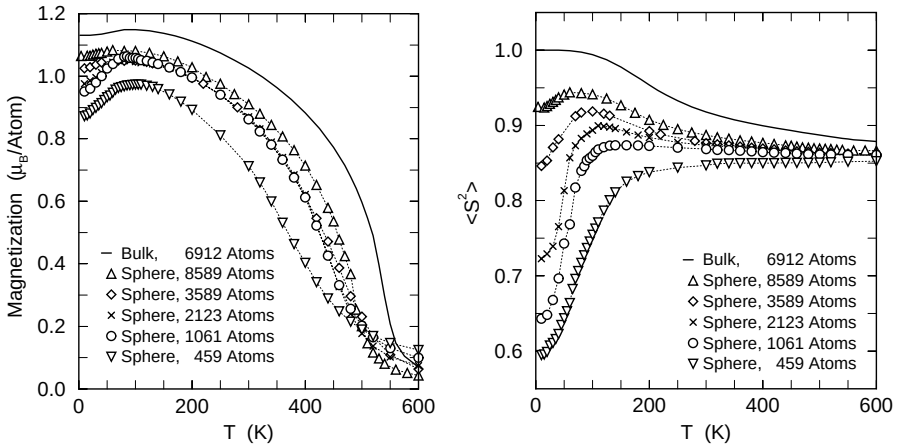

Figure 2. **Left:** Temperature dependence of the average magnetic moment for bulk and various particle sizes. **Right:** Temperature dependence of the averaged squared spin variable for different particle sizes.

size. The calculations were carried out for spherical particles ranging from 459 to 8589 atoms, which corresponds to diameters of 20 Å to 56 Å, respectively. In a second step we vary the concentration while keeping the particle size fixed to 1061 atoms (≈ 28 Å in diameter).

4.1 Magnetoelastic behavior depending on the size of the particles

The left panel of Fig. 2 shows the dependence of the magnetization on the particle size. The magnetization is given by the thermal average of the sum over the individual spins, multiplied with a factor of $2.8\,\mu_{\mathrm{B}}$ in case of an iron spin and $0.6\,\mu_{\mathrm{B}}$ for a nickel spin, respectively. As expected we find a decrease of the onset of magnetic order for smaller particles. This effect is due to the increasing fraction of surface atoms which have a smaller coordination number than bulk atoms. At low temperatures we find a slight dip in the magnetization which becomes more eminent for smaller particles. In bulk and in large particles the large and negative Fe-Fe exchange interaction which is in competition with the ferromagnetic Fe-Ni and Ni-Ni interactions causes a fraction of iron atoms to prefer antiferromagnetical alignment to the main spin direction as can be seen in Fig. 1 (upper part), which leads to a reduction of the net magnetization. On the surface, however, another mechanism can be observed,

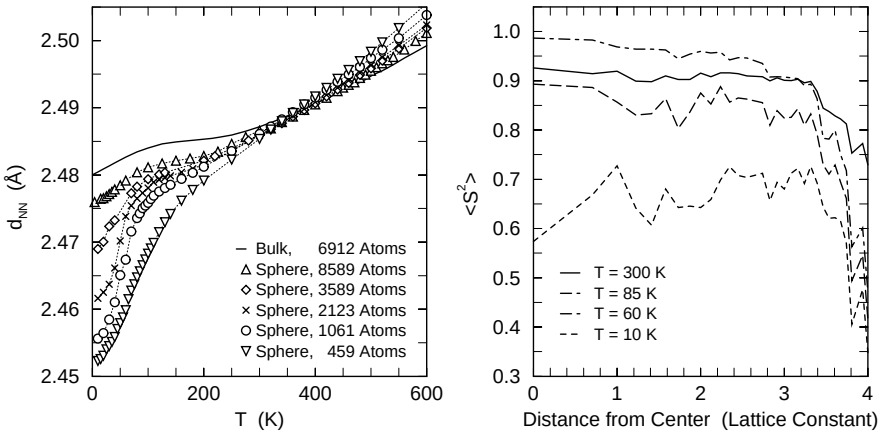

Figure 3. **Left:** Distance between nearest neighbors as a function of temperature. **Right:** Mean magnetic moment as a function of the distance to the center of the sphere at different temperatures. The values were averaged over particles with 1061 atoms but different distributions of the iron and nickel atoms.

which is dominating the behavior of small particles: In contrast to the bulk calculations, where periodic boundary conditions have been used, the reduced coordination on the surface allows for spatial relaxation of the atoms. Therefore, switching to the LM state, which comes along with potentials with a smaller equilibrium distance between the atoms causing energetically expensive lattice strains, becomes a feasible way for iron atoms on the surface to avoid magnetic frustrations induced by the competing exchange interactions.

This view is underlined by the right panel of Fig. 2 which shows the temperature dependence of the average of the squared spin variable giving the concentration of HM atoms in the system, which is also a measure for the mean magnetic moment of the atoms. In the bulk system we find that the fraction of LM atoms is vanishing at low temperatures, then gradually growing towards the high temperature limit of 13 %. Therefore, a growing number of elastic interactions appear with increasing temperature, which are described by the LM potentials characterized by a smaller lattice constant. This leads to a reduction of the mean neighbor distance compared to the pure HM case. For bulk $Fe_{65}Ni_{35}$ this reduction compensates the thermal expansion in a broad range of temperatures as it is observed in experiment (Fig. 3 left).

The Fe-Ni nanoparticles contain at low temperatures a considerable

amount of nonmagnetic iron spins which is growing with decreasing particle size. With increasing temperature the mean magnetic moment is rising, eventually passing through a slight maximum before approaching the high-temperature limit as in the bulk case. The increase of the magnetic moment causes the Invar effect to vanish and – for small particles – accounts for a largely enhanced thermal expansion, i.e. a pronounced anti-Invar behavior.

In order to shed further light on the mechanisms causing the rapid change of the mean magnetic moment, a profile of the distribution of HM atoms with respect to the distance from the center for different temperatures is given in Fig. 3 (right). Here we have considered a cluster of size 1061 atoms. From the figure we observe that at very low temperature (around $T = 10\,\mathrm{K}$) a considerable amount of atoms on the surface and in the inner part of the cluster have switched to the LM state. As the temperature is increased to $T = 60\,\mathrm{K}$ or $T = 85\,\mathrm{K}$ the bulk atoms favor the HM state and the surface atoms remain in the LM state. At higher temperatures (around $T = 300\,\mathrm{K}$) due to thermal fluctuations the concentration of HM atoms decreases in the bulk, whereas it increases on the surface causing a reduction in the difference between surface and core moment. From the study of the variation of the profile of the distribution of HM atoms with the temperature it seems that for small clusters the lattice spacing and the spin states on the surface and in the bulk are correlated at very low temperature, where the correlation length is larger than the system size. When we increase the temperature the correlation length decreases and above some particular temperature it becomes smaller than the system size, which leads to an uncorrelated dynamics of spin and lattice degrees of freedom of the surface and the bulk. Thus for small clusters one can expect a sudden change in HM concentrations and lattice distortions in the low temperature region contrary to the bulk Invar alloys. A reasonable microscopic interpretation for this behavior is that for small particles the small distortions on the lattice spacing on the surface caused by iron atoms which have switched to the LM state penetrate the whole particle (Fig. 1 lower part), leading to a smaller energy due to a reduction of unsatisfied antiferromagnetic Fe-Fe couplings. In large particles and in bulk, however, there are fewer possibilities to achieve a distorted but energetically favorable configuration, so that the nickel atoms, which can not accustom to a reduced lattice constant by changing their moments, stabilize the HM state (Fig. 1 upper part). For increasing temperatures, thermal fluctuations and anharmonic lattice vibrations make the LM state less favorable due to its preferred smaller lattice spacing. This will happen first in the core part of the particle because of the higher coordination number of the atoms. On the surface, however, there are more possibilities for the Fe atoms to stay close enough to

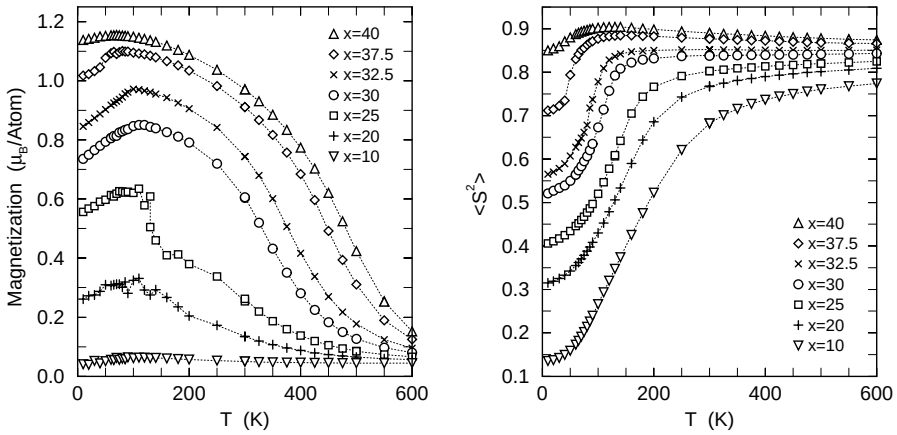

Figure 4. **Left:** Magnetization as a function of temperature for different compositions of $Fe_{1-x}Ni_x$ and fixed particle size of 1061 atoms. **Right:** Temperature dependence of the averaged squared spin variable for different nickel concentrations x.

their neighbors to avoid unsatisfied antiferromagnetic couplings by becoming nonmagnetic.

4.2 Composition-dependent properties of Fe-Ni particles

The magnetoelastic behavior of the Fe-Ni alloy shows a remarkable dependence on the Fe-Ni compositions (Fig. 4 left). For 40 at.% Ni Fig. 4 corresponds to the result expected for a pure ferromagnet and shows a dip in the magnetization at low temperature with the increase of the iron content because the anti-ferromagnetic Fe-Fe interaction destabilizes the ferromagnetic order. If the nickel content falls below 20 at.% ferromagnetism breaks down completely due to the almost complete loss of iron moment at low temperature (right panel of Fig. 4). At higher nickel concentration this loss of iron moment is less pronounced. Moreover from Fig. 4 we observe an increase of magnetic moment from a low value with the increasing temperature. The slope of this increase in moments seems to be maximum around the Invar concentration which is 35 at.%.

Again the behavior of the average moment is directly reflected in the change of the particle volume (Fig. 5 left) leading to a strong anti-Invar behavior over a wide range of temperatures, especially for low nickel concentrations. For higher nickel concentrations the specific heat (Fig. 5 right)

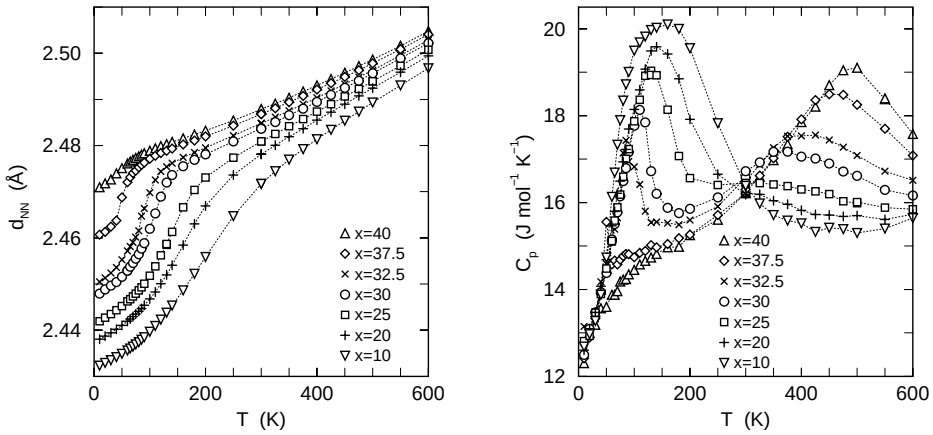

Figure 5. **Left:** Average nearest neighbor distance as a function of temperature for different compositions of $Fe_{1-x}Ni_x$. **Right:** Specific heat C_p as a function of temperature for different compositions of $Fe_{1-x}Ni_x$.

shows a pronounced maximum above $T = 400$ K, which corresponds to a breakdown of ferromagnetic order. With growing iron content this anomaly becomes increasingly washed out due to the weakening of ferromagnetism by the increasing number of antiferromagnetic Fe-Fe interactions in the particle and vanishes around 20 at.% Ni. At the same time a Schottky-type anomaly evolves below $T = 200$ K, which is located where the curve of the average particle moment and the average neighbor distance have their maximum slope. This maximum refers to the thermal excitation of HM atoms from the LM dominated ground state.

5 Conclusions

Our results underline that the transition from bulk to small particles or clusters account for a qualitative change of the properties of the material, which makes it extremely difficult to extrapolate the behavior of small particles from bulk properties. In the case of $Fe_{65}Ni_{35}$ the increasing surface to volume ratio causes the ground state of the particle to change so that the compensation of thermal expansion typical for Invar alloys turns into a largely enhanced volume expansion. However, our results imply that it is necessary to study particles of less than 10 nm in diameter in order to find a behavior that differs significantly from the bulk behavior. Unfortunately to the authors' knowl-

edge, so far no experimental measurements of the magnetoelastic properties of Fe-Ni clusters of a few nanometers in diameter have been made, which would allow for a comparison with our theoretical predictions.

One crucial point of the calculations presented in this paper is, that a phenomenological model has been used to describe the anomalous behavior of Fe-Ni alloys. This approach presupposes the availability of a reasonable set of parameters. For bulk calculations these can be obtained from numerous experimental measurements and *ab initio* investigations. For particles and clusters, however, it can be expected that due to the reduced coordination of the surface atoms, the bulk parameters have to be modified in order to meet the situation on the surface correctly. *Ab initio* calculations of Fe-Ni surfaces can help to fix the surface parameters, but in order to account for magnetovolume effects, the possibility of a spatial relaxation of the surface atoms has to be included. This will make *ab initio* calculations computationally expensive, especially for disordered materials. Furthermore, regarding small clusters containing about 1000 atoms or less, our results let suspect that this relaxation takes place throughout the whole particle, which also makes it difficult to extrapolate from *ab initio* bulk and surface results the electronic properties of small clusters and particles.

Acknowledgements

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